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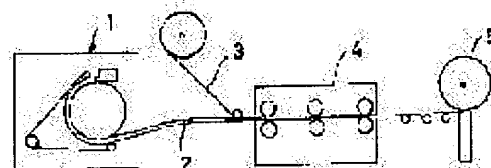
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### (54) ELECTRODE PLATE FOR LEAD-ACID BATTERY AND LEAD-ACID BATTERY USING THE ELECTRODE PLATE

(57)Abstract:

PURPOSE: To improve the adhesive property of a grid and an active material, and to increase the service life property, by making a part or the whole body of the crystal formation inside a grid alloy to a recrystallization formation, after filling a paste to be an active material to a grid body prior to the recrystallization.

CONSTITUTION: A slab made of a Pb-Ca-Sn alloy casted by a slab casting machine 1, and a Pb-Sb-Sn alloy foil 3 are delivered to a rolling machine 4 in the condition superposing both members, so as to be rolled, and a lead alloy sheet 5 on which the Pb-Sb-Sn alloy is coated is obtained. And after the sheet 5 is produced, it is expanding processed as in the condition the crystal formation is the rolled formation, a paste is filled, a heat treatment at 60°C or higher is applied, and a part of the grid formation is recrystallized. As a result, when the grid in the rolled formation condition is transferred to the recrystallization formation partially by the heat in the aging drying of the grid, the grid is contracted to a specific height. In such a way, the active material and the grid are adhered strongly, and the service life property is improved.



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(54)【発明の名称】 鉛蓄電池用極板とこれを用いた鉛蓄電池

(57)【要約】

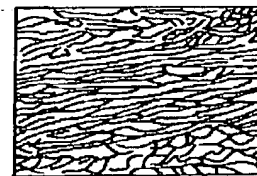
【目的】 鉛-カルシウム-錫系合金の圧延シートをエキスパンド加工した格子を用いた電池の寿命、特に高温下での寿命特性の改善を目的とする。

【構成】 鉛-カルシウム-錫系合金のスラブを120℃以下の温度で冷間圧延し、合金内部に緻密な圧延組織をもつ鉛合金シートとし、再結晶化前にこれをエキスパンド加工などの機械加工を施して格子体とし、活物質となるペーストを充填した後、格子合金内部の結晶組織の一部または全部を再結晶組織とさせた極板を鉛蓄電池用極板として用いる。

(A)



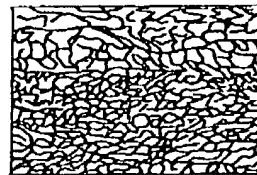
(B)



(C)



(D)



## 【特許請求の範囲】

【請求項1】 鉛-カルシウム-錫系合金のスラブを120℃以下の温度で冷間圧延し、合金内部に緻密な圧延組織をもつ鉛合金シートとし、再結晶化前にこれをエキスパンド加工などの機械加工を施して格子体とし、活物質となるペーストを充填した後、格子合金内部の結晶組織の一部または全部を再結晶組織とさせた鉛蓄電池用極板。

【請求項2】 活物質となるペーストを充填した後、60℃以上の温度で熱処理を行って格子合金内部の結晶組織の一部または全部を再結晶組織とさせたことを特徴とする請求項1記載の鉛蓄電池用極板。

【請求項3】 添加する錫の濃度を0.5~2.0%、カルシウムの濃度を0.05~0.08%の範囲としたことを特徴とする請求項1または2記載の鉛蓄電池用極板。

【請求項4】 化成後の体積が化成前の体積と比べて1%以上増加するようなペーストを用いたことを特徴とする請求項1乃至3のいずれかに記載の鉛蓄電池用極板。

【請求項5】 陽極板として用いることを特徴とする請求項1乃至4のいずれかに記載の鉛蓄電池用極板。

【請求項6】 前記請求項1乃至5のいずれかに記載の鉛蓄電池用極板を用いたことを特徴とする鉛蓄電池。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は鉛蓄電池の改良、特に陽極格子に鉛-カルシウム-錫系合金を用いたメンテナンスフリータイプ、いわゆるCa系鉛蓄電池の寿命特性の改善、特に高温寿命特性の改善に関するものである。

## 【0002】

【従来の技術】陽陰極格子体に鉛-カルシウム-錫系合金を用いた鉛蓄電池は自己放電が少ないことや保存特性が優れていることなどの特徴を有しメンテナンスフリー電池と呼ばれている。

【0003】このような合金系を格子に用いる電池において、圧延した錫合金シートをエキスパンド加工し格子体とする方法がそれまでの鋳造法にとって代わり、広く普及している。

【0004】しかしながら、このような鉛-カルシウム-錫系合金を陽極に用いた鉛蓄電池は、陽極に鉛-アンチモン系合金を使用した電池と比べ格子と活物質の密着性の低下に由来する電池性能の低下を生じやすいことが一般に知られている。

【0005】この原因の一つとして使用中に陽極格子が酸化腐食する過程で体積膨張し、そのために格子全体が変形することにより、活物質と格子の間に空隙を生ずる事があげられる。

【0006】またもう一つの原因は格子にアンチモンが含まれていると、それが使用中に徐々に活物質中に溶け出し活物質と格子の密着性を良好にするが、鉛-カルシ

ウム-錫系合金にはアンチモンが含まれていないことも影響する。前者の原因を解決する一つの方法は格子合金の耐酸化性をより向上し、また酸化して体積膨張する力に打ち勝てるように引張強度の高い合金を用意する事である。これについては、鉛-カルシウム-錫系合金中の錫濃度を2.0%以内の範囲で高くしていくことが有効な手段であることが分かってきた。

【0007】後者の原因を解決する手段としては鉛合金シートの表面に鉛-アンチモン系合金を張りつけるなどの方法が考案されている。

## 【0008】

【発明が解決しようとする課題】このように鉛-カルシウム-錫系合金を陽極格子体に用いる電池では、今まで、格子と活物質の密着性を物理的にあるいは化学的にいかに向上させるかに改善の努力が傾注されてきた。本発明は格子と活物質の密着性をこれまでとは異なった原理により物理的に向上させ、寿命特性、特に高温での寿命特性の改善を図ることを目的とする。

## 【0009】

【課題を解決するための手段】本発明の鉛蓄電池用電極は、前記目的を達成するべく、鉛-カルシウム-錫系合金のスラブを120℃以下の温度で冷間圧延し、合金内部に緻密な圧延組織をもつ鉛合金シートとし、再結晶化前にこれをエキスパンド加工などの機械加工を施して格子体とし、活物質となるペーストを充填した後、格子合金内部の結晶組織の一部または全部を再結晶組織とさせたものであり、また、本発明の鉛蓄電池は前記鉛蓄電池用電極を電極として用いるものである。

【0010】前記再結晶化は、活物質となるペーストを充填した後、60℃以上の温度で熱処理を行って格子合金内部の結晶組織の一部または全部を再結晶組織とさせるのが好ましい。

【0011】また、添加する錫の濃度を0.5~2.0%、カルシウムの濃度を0.05~0.08%の範囲とするのが好ましい。

【0012】また、前記ペーストとして化成後の体積が化成前の体積と比べて1%以上増加するようなペーストを用いるのが好ましい。

【0013】また、前記鉛蓄電池用電極は陽極板として用いるのが好ましい。また、前記鉛合金シートの表面あるいは表面の一部に鉛-アンチモン-錫系合金を付与することにより、寿命をより向上させることができる。

## 【0014】

【作用】冷間圧延された鉛-カルシウム-錫系合金は圧延直後は緻密な圧延組織をもつ。この組織は時間経過とともに安定な再結晶性組織へと変化する。この変化は温度が高いほど早く起こる。この再結晶組織の形成と共に結晶組織の粒界には鉛とカルシウムあるいは錫とカルシウムの化合物が生成してきて鉛合金シートの機械的な強度が向上する。今回この鉛-カルシウム-錫系合金の圧

延シートが再結晶組織に変化する時、わずかに格子が収縮を起こすことが実験の結果より推定された。従って、再結晶前にこの鉛合金シートをエキスパンド加工などにより格子体とし、ペーストを充填した後、この格子体を再結晶させることにより格子体自身がわずかに収縮を起こし格子と活物質が機械的に強く密着されることが分かった。

【0015】また活物質も化成時の膨張が大きくなるように選択すると、より格子と活物質との機械的な密着力を高めることができる。化成時の膨張を大きくするためには例えばペースト中に鉛丹を添加することなどが有効である。

【0016】このような効果をもっとも発揮し実際に寿命向上に効果のある合金組成は錫の濃度が0.5~2.0%、カルシウムの濃度が0.05~0.08%のあいだであった。さらに鉛合金シートの表面あるいは表面の一部に鉛-アンチモン-錫系合金を付与したものについて同様の処理を行うと化学的な格子と活物質の密着性の向上も同時に図れるためによりいっそうの寿命向上の効果がある。

【0017】

【実施例】以下実施例により、本発明について説明する。

(実験1) 鉛-0.07%カルシウム-1.0%錫合金を溶解し、それを厚さ10mm、幅80mmのスラブとした後、圧延して厚さ1.0mmの圧延シートとした。

【0018】また同一組成で表面に鉛-5%アンチモン-5%錫合金をコーティングした圧延シートも同時に作\*

\*製した。このときのシートの作製方法を図1に、また作製したシートから得られた鉛蓄電池用極板の概略図を図2に示す。

【0019】図1に示すように、スラブ鋳造機1で鋳造されたPb-Ca-Sn合金製スラブ2とPb-Sb-Sn合金箔3を重ね合わせた状態で圧延機4に送り込んで圧延し、Pb-Sb-Sn合金をコーティングした鉛合金シート5を得た。

【0020】図2中、11は極板、12はエキスパンド格子骨を示し、図中Aで示される格子骨の拡大断面では、13がPb-Sb-Sn合金コーティング層、14がPb-Ca-Sn合金格子骨を示す。

【0021】これらのシートについて一部はシート状態で60℃中に48時間放置した。このとき圧延組織の一部は再結晶組織に変化した。この状態でエキスパンド加工し、ペーストを充填して極板とした。また他の一部についてはシート作製後結晶組織が圧延組織の状態のままでエキスパンド加工を行いペーストを充填しその後60℃で48時間の熱処理を行い格子の一部の組織を再結晶させた。このような極板を用いて電池を作製し75℃でJIS D 5301の軽負荷寿命試験を行った。その結果を表1に示す。このとき鉛粉には通常の鉛酸化物と金属鉛からなる粉末のほかに鉛丹を80%含む鉛酸化物の粉体を20%含むものを用い、これを定法に従い、水と希硫酸とで混練しペースト状としたものを用いた。

【0022】

【表1】

| 電池No | 極板の製造方法           | コーティング | 寿命回数 |
|------|-------------------|--------|------|
| A    | 圧延組織のまま<br>で格子に加工 | なし     | 4200 |
| B    | 圧延組織のまま<br>で格子に加工 | あり     | 7000 |
| C    | 再結晶組織後<br>を格子に加工  | なし     | 1800 |
| D    | 再結晶組織後<br>を格子に加工  | あり     | 2400 |

【0023】表1の結果のように圧延組織の状態のままの鉛シートをエキスパンド加工し、その後熱乾燥したときに格子が再結晶した極板を用いた電池(A、B)のほうが鉛シートを熱処理し、部分的に再結晶組織としたものをエキスパンド加工しペーストを充填し極板とした電池(C、D)と比べて寿命が格段に長く、またそのなかでもシート表面に鉛-アンチモン系合金をコーティングした場合のほうが寿命が長いことが分かる。この時、極板の高さを測定すると熱乾燥後ではA、Bの極板は乾燥前より1.2mm収縮していたのに対し、C、Dで※50

※は0.5mmしか収縮していなかった(初期の極板の高さは100mm)。また、化成後の高さはA、Bでは化成前より1.0mm、すなわち約1%伸びて初期より0.2mm収縮していたのに対して、C、Dでは化成前より1.0mm伸びて初期より0.5mm伸びていたのが観察された。

【0024】以上のことから、圧延組織の状態の格子が熱乾燥のときの熱により部分的に再結晶組織に移行するときに格子は高さ方向に収縮するような形状変化をすることが分かる。この結果、活物質と格子が強く密着さ

れるような力が働きこのことにより、寿命が向上すると考えられる。また、極板は化成後に体積膨張を起こすが、このことと相まってより格子と活物質の密着性が向上するものと考えられる。

【0025】なお、電池A、Bにおけるシートの組織、すなわち圧延組織と、電池C、Dにおけるシートの組織、すなわち部分的に再結晶組織となっている状態を図3の模式図に示す。また合わせてそれぞれの電池の格子の金属組織を同時に示すがどちらも部分的に再結晶組織になっていることが分かる。

(実験2) この化成時の活物質の膨張による効果を調べるためにペーストの処方を変え、化成前後の体積変化が異なるような活物質による比較を行った。表2に、寿命\*

\*が最も長かった電池Bの条件でペーストを通常の鉛酸化物粉と金属鉛粉とからなる鉛粉のみで作った電池Eと、比較のために電池Dの条件で同一ペーストを用いた電池Fの寿命試験結果を示す。寿命試験の結果は対応する電池B、Dに対してE、Fとも短くなっており、とくにBに対するEの寿命の低下が大きかった。極板の高さ変化を測定すると熱成乾燥後ではE、Fの極板の収縮はBおよびDと同じであったが、化成後の伸びは化成前より0.5mm、すなわち約0.5%にしか過ぎなかった。

このことにより、化成後の活物質の体積膨張が1%以上であることにより、より効果があることが分かった。

【0026】

【表2】

| 電池No | 極板の製造方法           | コーティング | 寿命回数 | 備考           |
|------|-------------------|--------|------|--------------|
| E    | 圧延組織のまま<br>で格子に加工 | あり     | 4000 | B、Dとペーストが異なる |
| F    | 再結晶組織後<br>を格子に加工  | あり     | 2000 |              |

【0027】さらに詳しく調べるため、鉛-カルシウム-錫系合金の組成別に寿命の変化を調べた。その結果を図4に示す。この図から錫およびカルシウムの添加量により寿命は著しく変化することが分かる。これはそれぞれの合金組成での耐食性および機械的強度によるものである。この図より錫の濃度範囲としては0.5~2.0%、カルシウムの濃度範囲としては0.05~0.08%の範囲が適当なことが分かる。

【0028】また本発明では、以上述べたように、鉛シートの状態では圧延組織で、格子の状態では再結晶組織を形成することが肝要であるが、鉛シートの状態で再結晶組織を形成しないためには圧延加工を120℃以下の温度で行うことが有効であることも別の実験で確かめられた。

【0029】

【発明の効果】以上のように本発明によれば、鉛-カルシウム-錫系合金の圧延シートにエキスパンド加工などの機械加工を施して得た格子体を用いる鉛蓄電池の高温下での寿命を顕著に改善できる。

【図面の簡単な説明】

※【図1】表面にPb-Sb-Sn合金をコーティングしながらPb-Ca-Sn合金を圧延し鉛合金シートを製作する工程の模式図

【図2】前記鉛合金シートから得られた鉛蓄電池用極板の概略図

【図3】各電池に用いた鉛合金シートおよび格子骨の結晶状態を示す模式図

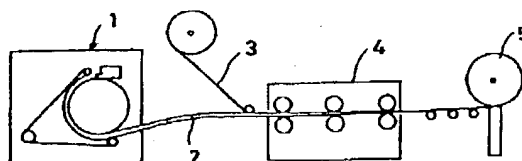
【図4】CaおよびSn濃度と寿命試験回数との関係を示す特性図

【符号の説明】

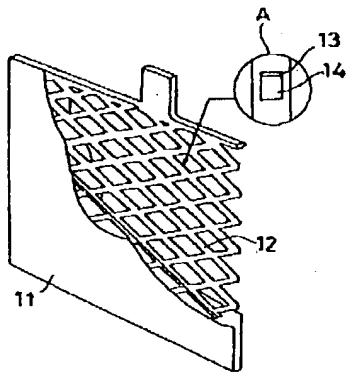
- 1 スラブ製造機
- 2 Pb-Ca-Sn合金製スラブ
- 3 Pb-Sb-Sn合金箔
- 4 圧延機
- 5 鉛合金シート
- 11 極板
- 12 エキスパンド格子骨
- 13 Pb-Sb-Sn合金コーティング層
- 14 Pb-Ca-Sn合金格子骨

※40 A 格子骨断面

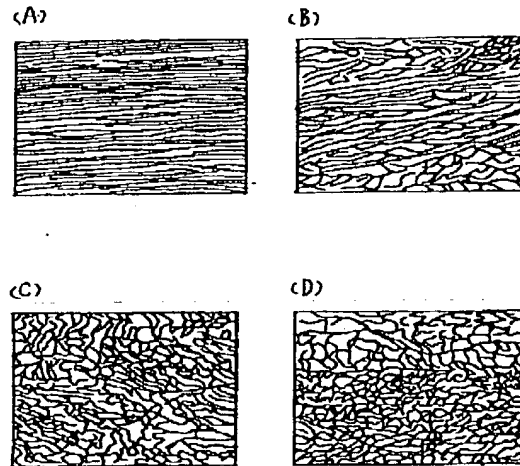
【図1】



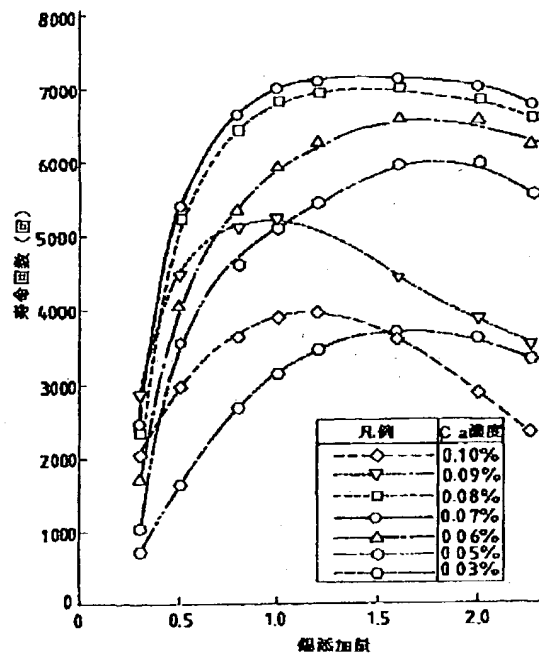
【図2】



【図3】



【図4】



フロントページの続き

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産業株式会社内

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CLAIMS

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[Claim(s)]

[Claim 1] A plate for lead accumulators which slab of a lead-calcium-tin system alloy is cold-rolled at temperature of 120 degrees C or less, and it considers as a lead alloy sheet which has a precise rolling organization in the interior of an alloy, expanded processing etc. is machined and this is made into a grid object before recrystallization, and made recrystallized structure some or all of the crystalline structure inside a grid alloy after being filled up with a paste used as an active material.

[Claim 2] A plate for lead accumulators according to claim 1 characterized by having heat-treated at temperature of 60 degrees C or more, and making some or all of the crystalline structure inside a grid alloy into recrystallized structure after being filled up with a paste used as an active material.

[Claim 3] A plate for lead accumulators according to claim 1 or 2 characterized by making concentration of calcium into 0.05 - 0.08% of range for concentration of tin to add 0.5 to 2.0%.

[Claim 4] formation -- a plate for lead accumulators according to claim 1 to 3 characterized by using a paste which increases 1% or more compared with volume before next volume degassing.

[Claim 5] A plate for lead accumulators according to claim 1 to 4 characterized by using as an anode plate.

[Claim 6] A lead accumulator characterized by using said plate for lead accumulators according to claim 1 to 5.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to an improvement of the so-called life property of amelioration of a lead accumulator especially the maintenance-free type which used the lead-calcium-tin system alloy for the anode plate grid, and calcium system lead accumulator, especially an improvement of an elevated-temperature life property.

[0002]

[Description of the Prior Art] The lead accumulator which used the lead-calcium-tin system alloy for the positive cathode grid object has the features, like there being little self-discharge and a conservation property are excellent, and is called the maintenance-free cell.

[0003] For the casting till then, and the method of carrying out expanded processing of the tin alloy sheet which rolled out such an alloy system in the cell used for a grid, and using as a grid object is large, and has spread.

[0004] However, generally it is known that the lead accumulator which used such a lead-calcium-tin system alloy for the anode plate will tend to produce the cell performance degradation which originates in the fall of the adhesion of a grid and an active material compared with the cell which used the lead-antimony system alloy for the anode plate.

[0005] When cubical expansion is carried out in the process in which an anode plate grid carries out oxidation corrosion during use as one of the cause of this, therefore the whole grid deforms, producing an opening is raised between an active material and a grid.

[0006] Moreover, although another cause will begin to melt into an active material gradually and will make adhesion of an active material and a grid good while it uses it if antimony is contained in the grid, that antimony is not contained also influences a lead-calcium-tin system alloy. The one method of solving the former cause is preparing an alloy with high tensile strength so that the force which improves more, and oxidizes and carries out cubical expansion of the oxidation resistance of a grid alloy can be overcome. About this, it has turned out that it is an effective means to make high tin concentration in a lead-calcium-tin system alloy in less than 2.0% of range.

[0007] Methods, such as sticking a lead-antimony system alloy on the surface of a lead alloy sheet as a means to solve the latter cause, are devised.

[0008]

[Problem(s) to be Solved by the Invention] Thus, by the cell which uses a lead-calcium-tin system alloy for an anode plate grid object, efforts for an improvement have been concentrated on how [ physically or / chemical ] the adhesion of a grid and an active material is raised until now. This invention raises the adhesion of a grid and an active material physically by different principle from the former, and it aims at aiming at an improvement of a life property, especially the life property in an elevated temperature.

[0009]

[Means for Solving the Problem] An electrode for lead accumulators of this invention cold-rolls slab of a lead-calcium-tin system alloy at temperature of 120 degrees C or less so that it may attain said purpose. Consider as a lead alloy sheet which has a precise rolling organization in the interior of an alloy, and before recrystallization, machine expanded processing etc. and this is made into a grid object. After being filled up with a paste used as an active material, some or all of the crystalline structure inside a grid alloy is made into recrystallized structure, and a lead accumulator of this invention uses said electrode for lead accumulators as an electrode.

[0010] After said recrystallization is filled up with a paste used as an active material, it is desirable to heat-treat at temperature of 60 degrees C or more, and to make some or all of the crystalline structure inside a grid alloy into recrystallized structure.

[0011] Moreover, it is desirable to make concentration of calcium into 0.05 - 0.08% of range for concentration of tin to add 0.5 to 2.0%.

[0012] moreover -- as said paste -- formation -- it is desirable to use a paste which increases 1% or more compared with volume before next volume degassing.

[0013] Moreover, as for said electrode for lead accumulators, using as an anode plate is desirable. Moreover, a life can be raised more by giving a lead-antimony-tin system alloy to a part of surface of said lead alloy sheet, or surface.

[0014]

[Function] The cold-rolled tin-calcium-tin system alloy has a precise rolling organization immediately after rolling. This organization changes to a stable recrystallization nature organization with time amount progress. This change takes place early, so that temperature is high. With formation of this recrystallized structure, in the grain boundary of the crystalline structure, the compound of lead, calcium, or tin and calcium generates, and the mechanical reinforcement of a lead alloy sheet improves. When the rolling sheet of this lead-calcium-tin system alloy changed to recrystallized structure this time, it was presumed from the result of an experiment that a grid causes contraction slightly. Therefore, after using this lead alloy sheet as the grid object by expanded processing etc. and being filled up with the paste before recrystallization, by making this grid object recrystallize showed that contraction was slightly stuck on the grid object itself to a lifting grid and an active material strongly mechanically.

[0015] moreover, an active material -- formation -- if it chooses so that the expansion at the time may become large, the mechanical adhesion force of a grid and an active material can be heightened more. formation -- in order to enlarge expansion at the time, it is effective for example, during a paste to add a minium etc.

[0016] the alloy presentation which demonstrates such an effect most and actually has an effect in the improvement in a life was, while the concentration whose concentration of tin is 0.5 - 2.0% and calcium was 0.05 - 0.08%. Since improvement in the adhesion of a chemical grid and an active material can also be aimed at to coincidence if processing same about what furthermore gave the lead-antimony-tin system alloy to a part of surface of a lead alloy sheet or surface is performed, there is an effect of much more improvement in a life.

[0017]

[Example] Below, an example explains this invention.

(Experiment 1) After dissolving the tin alloy -0.07% calcium-1.0% of lead and making it into slab with 10mm [ in thickness ], and a width of face of 80mm, it rolled out and considered as the rolling sheet with a thickness of 1.0mm.

[0018] Moreover, the rolling sheet which coated the surface with the tin alloy by the same presentation -5% antimony-5% of lead was also produced to coincidence. The schematic diagram of the plate for lead accumulators obtained from the sheet which produced the production method of the sheet at this time to drawing 1 again is shown in drawing 2.

[0019] As shown in drawing 1, where the slab 2 made from a Pb-calcium-Sn alloy and the Pb-Sb-Sn alloy foil 3 which were cast in the slab casting machine 1 are piled up, it sent in and rolled out to the rolling mill 4, and the lead alloy sheet 5 which coated the Pb-Sb-Sn alloy was obtained.

[0020] By the enlarged section of the grid bone which 11 show a plate among drawing 2, and 12 shows an expanded metal grating bone, and is shown all over [ A ] drawing, 13 shows a Pb-Sb-Sn alloy coating layer, and 14 shows a Pb-calcium-Sn alloy grid bone.

[0021] The part was left in 60 degrees C in the state of the sheet about these sheets for 48 hours. At this time, some rolling organizations changed to recrystallized structure. Expanded processing was carried out in this condition, and it was filled up with the paste and considered as the plate. Moreover, about other parts, while the crystalline structure after sheet production had been in the condition of a rolling organization, expanded processing was performed, it was filled up with the paste, heat treatment of 48 hours was performed at 60 degrees C after that, and the organization of a part of grid was made to recrystallize. A cell is produced using such a plate and it is JIS at 75 degrees C. D Light load life test of 5301 was performed. The result is shown in a table 1. what contains in lead powder the fine particles of the plumbic acid ghost which contains the minium other than the powder which consists of a usual plumbic acid ghost and metal lead 80% 20% at this time --

using -- this -- a law -- according to the method, what kneaded with water and a dilute sulfuric acid and was made into the shape of a paste was used.

[0022]

[A table 1]

| 電池 N O | 極板の製造方法           | コーティング | 寿命回数    |
|--------|-------------------|--------|---------|
| A      | 圧延組織のまま<br>で格子に加工 | なし     | 4 2 0 0 |
| B      | 圧延組織のまま<br>で格子に加工 | あり     | 7 0 0 0 |
| C      | 再結晶組織後を<br>格子に加工  | なし     | 1 8 0 0 |
| D      | 再結晶組織後を<br>格子に加工  | あり     | 2 4 0 0 |

[0023] Expanded processing of the lead sheet with the condition of a rolling organization is carried out like [ as a result of a table 1 ]. The way of the cell (A, B) using the plate which the grid recrystallized when aging desiccation was carried out after that heat-treats a lead sheet. compared with the cell (C, D) which carried out expanded processing of what was partially made into recrystallized structure, was filled up with the paste and used as the plate, a life is markedly alike, it is long and a \*\*\*\*\* understands [ the way at the time of coating the sheet surface with a lead-antimony system alloy also in it ] a life. At this time, when the height of a plate was measured, by C and D, it had contracted only 0.5mm to having contracted the plate of A and B 1.2mm from desiccation before after aging desiccation (the height of an early plate is 100mm). moreover, formation -- next height -- A and B -- formation -- a front -- 1.0mm, i.e., it was extended about 1% and had contracted 0.2mm from the first stage, -- receiving -- C and D -- formation -- it was extended 1.0mm from the front and having been extended 0.5mm was observed from the first stage.

[0024] When shifting to recrystallized structure partially from the above thing with heat in case the grid of the condition of a rolling organization is aging desiccation, it turns out that a grid carries out configuration change which is contracted in the height direction. Consequently, force which is strongly stuck to an active material and a grid works, and it is thought that a life improves by this. moreover, a plate -- formation -- although cubical expansion is caused behind, it is thought that the adhesion of a grid and an active material improves more conjointly with this.

[0025] In addition, the organization of the sheet in Cells A and B, i.e., a rolling organization, and the organization of the sheet in Cells C and D, i.e., the condition of being recrystallized structure partially, are shown in the mimetic diagram of drawing 3 . Moreover, although it doubles and the metal texture of the grid of each cell is shown in coincidence, it turns out that both are recrystallized structure partially.

(Experiment 2) this formation -- in order to investigate the effect by expansion of the active material at the time -- the formula of a paste -- changing -- formation -- the comparison by active material with which volume changes [ before and after ] differ was performed. The life test result of the cell E by which the life made the paste only from the lead powder which consists of usual plumbic acid ghost powder and metal lead powder on condition that the longest cell B, and the cell F which used the same paste on condition that Cell D sake [ comparison-] is shown in a table 2. E and F were short to the corresponding cells B and D, and the result of life test had the large fall of the life of E especially to B. although contraction of the plate of E and F was the same as B and D after aging desiccation when height change of a plate was measured -- formation -- next elongation -- formation -- it did not pass from a front to 0.5mm, i.e., about 0.5%. this -- formation -- when the cubical expansion of a next active material is 1% or more showed that it was more effective.

[0026]

[A table 2]

| 電池 N O | 極板の製造方法           | コーティング | 寿命回数    | 備考                     |
|--------|-------------------|--------|---------|------------------------|
| E      | 圧延組織のまま<br>で格子に加工 | あり     | 4 0 0 0 | B, D とペ<br>ーストが異<br>なる |
| F      | 再結晶組織後<br>を格子に加工  | あり     | 2 0 0 0 |                        |

[0027] In order to investigate in more detail, change of a life was investigated according to the presentation of a lead-calcium-tin system alloy. The result is shown in drawing 4. The addition of tin and calcium shows that a life changes remarkably from this drawing. This is based on the corrosion resistance in each alloy presentation, and a mechanical strength. This drawing shows that 0.05 - 0.08% of range is suitable as a density range of calcium 0.5 to 2.0% as a density range of tin.

[0028] Moreover, by this invention, as stated above, in the state of the lead sheet, it was important in the rolling organization to have formed recrystallized structure in the state of a grid, but in order not to form recrystallized structure in the state of a lead sheet, it was confirmed in another experiment that it is also effective to perform strip processing at the temperature of 120 degrees C or less.

[0029]

[Effect of the Invention] According to this invention, the life under the elevated temperature of the lead accumulator using the grid object which machined expanded processing etc. on the rolling sheet of a lead-calcium-tin system alloy, and was acquired on it is notably improvable as mentioned above.

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TECHNICAL FIELD

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[Industrial Application] This invention relates to an improvement of the so-called life property of amelioration of a lead accumulator especially the maintenance-free type which used the lead-calcium-tin system alloy for the anode plate grid, and calcium system lead accumulator, especially an improvement of an elevated-temperature life property.

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PRIOR ART

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[Description of the Prior Art] The lead accumulator which used the lead-calcium-tin system alloy for the positive cathode grid object has the features, like there being little self-discharge and a conservation property are excellent, and is called the maintenance-free cell.

[0003] For the casting till then, and the method of carrying out expanded processing of the tin alloy sheet which rolled out such an alloy system in the cell used for a grid, and using as a grid object is large, and has spread.

[0004] However, generally it is known that the lead accumulator which used such a lead-calcium-tin system alloy for the anode plate will tend to produce the cell performance degradation which originates in the fall of the adhesion of a grid and an active material compared with the cell which used the lead-antimony system alloy for the anode plate.

[0005] When cubical expansion is carried out in the process in which an anode plate grid carries out oxidation corrosion during use as one of the cause of this, therefore the whole grid deforms, producing an opening is raised between an active material and a grid.

[0006] Moreover, although another cause will begin to melt into an active material gradually and will make adhesion of an active material and a grid good while it uses it if antimony is contained in the grid, that antimony is not contained also influences a lead-calcium-tin system alloy. The one method of solving the former cause is preparing an alloy with high tensile strength so that the force which improves more, and oxidizes and carries out cubical expansion of the oxidation resistance of a grid alloy can be overcome. About this, it has turned out that it is an effective means to make high tin concentration in a lead-calcium-tin system alloy in less than 2.0% of range.

[0007] Methods, such as sticking a lead-antimony system alloy on the surface of a lead alloy sheet as a means to solve the latter cause, are devised.

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EFFECT OF THE INVENTION

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TECHNICAL PROBLEM

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MEANS

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[Means for Solving the Problem] An electrode for lead accumulators of this invention cold-rolls slab of a lead-calcium-tin system alloy at temperature of 120 degrees C or less so that it may attain said purpose. Consider as a lead alloy sheet which has a precise rolling organization in the interior of an alloy, and before recrystallization, machine expanded processing etc. and this is made into a grid object. After being filled up with a paste used as an active material, some or all of the crystalline structure inside a grid alloy is made into recrystallized structure, and a lead accumulator of this invention uses said electrode for lead accumulators as an electrode.

[0010] After said recrystallization is filled up with a paste used as an active material, it is desirable to heat-treat at temperature of 60 degrees C or more, and to make some or all of the crystalline structure inside a grid alloy into recrystallized structure.

[0011] Moreover, it is desirable to make concentration of calcium into 0.05 - 0.08% of range for concentration of tin to add 0.5 to 2.0%.

[0012] moreover -- as said paste -- formation -- it is desirable to use a paste which increases 1% or more compared with volume before next volume degassing.

[0013] Moreover, as for said electrode for lead accumulators, using as an anode plate is desirable. Moreover, a life can be raised more by giving a lead-antimony-tin system alloy to a part of surface of said lead alloy sheet, or surface.

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OPERATION

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[Function] The cold-rolled tin-calcium-tin system alloy has a precise rolling organization immediately after rolling. This organization changes to a stable recrystallization nature organization with time amount progress. This change takes place early, so that temperature is high. With formation of this recrystallized structure, in the grain boundary of the crystalline structure, the compound of lead, calcium, or tin and calcium generates, and the mechanical reinforcement of a lead alloy sheet improves. When the rolling sheet of this lead-calcium-tin system alloy changed to recrystallized structure this time, it was presumed from the result of an experiment that a grid causes contraction slightly. Therefore, after using this lead alloy sheet as the grid object by expanded processing etc. and being filled up with the paste before recrystallization, by making this grid object recrystallize showed that contraction was slightly stuck on the grid object itself to a lifting grid and an active material strongly mechanically.

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## EXAMPLE

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(Experiment 1) After dissolving the tin alloy -0.07% calcium-1.0% of lead and making it into slab with 10mm [ in thickness ], and a width of face of 80mm, it rolled out and considered as the rolling sheet with a thickness of 1.0mm.

[0018] Moreover, the rolling sheet which coated the surface with the tin alloy by the same presentation -5% antimony-5% of lead was also produced to coincidence. The schematic diagram of the plate for lead accumulators obtained from the sheet which produced the production method of the sheet at this time to drawing 1 again is shown in drawing 2.

[0019] As shown in drawing 1, where the slab 2 made from a Pb-calcium-Sn alloy and the Pb-Sb-Sn alloy foil 3 which were cast in the slab casting machine 1 are piled up, it sent in and rolled out to the rolling mill 4, and the lead alloy sheet 5 which coated the Pb-Sb-Sn alloy was obtained.

[0020] By the enlarged section of the grid bone which 11 show a plate among drawing 2, and 12 shows an expanded metal grating bone, and is shown all over [ A ] drawing, 13 shows a Pb-Sb-Sn alloy coating layer, and 14 shows a Pb-calcium-Sn alloy grid bone.

[0021] The part was left in 60 degrees C in the state of the sheet about these sheets for 48 hours. At this time, some rolling organizations changed to recrystallized structure. Expanded processing was carried out in this condition, and it was filled up with the paste and considered as the plate. Moreover, about other parts, while the crystalline structure after sheet production had been in the condition of a rolling organization, expanded processing was performed, it was filled up with the paste, heat treatment of 48 hours was performed at 60 degrees C after that, and the organization of a part of grid was made to recrystallize. A cell is produced using such a plate and it is JIS at 75 degrees C. D Light load life test of 5301 was performed. The result is shown in a table 1. what contains in lead powder the fine particles of the plumbic acid ghost which contains the minium other than the powder which consists of a usual plumbic acid ghost and metal lead 80% 20% at this time -- using -- this -- a law -- according to the method, what kneaded with water and a dilute sulfuric acid and was made into the shape of a paste was used.

[0022]

[A table 1]

| 電池 N o | 極板の製造方法           | コーティング | 寿命回数    |
|--------|-------------------|--------|---------|
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[0023] Expanded processing of the lead sheet with the condition of a rolling organization is carried out like [ as

a result of a table 1 ]. The way of the cell (A, B) using the plate which the grid recrystallized when aging desiccation was carried out after that heat-treats a lead sheet. compared with the cell (C, D) which carried out expanded processing of what was partially made into recrystallized structure, was filled up with the paste and used as the plate, a life is markedly alike, it is long and a \*\*\*\*\* understands [ the way at the time of coating the sheet surface with a lead-antimony system alloy also in it ] a life. At this time, when the height of a plate was measured, by C and D, it had contracted only 0.5mm to having contracted the plate of A and B 1.2mm from desiccation before after aging desiccation (the height of an early plate is 100mm). moreover, formation -- next height -- A and B -- formation -- a front -- 1.0mm, i.e., it was extended about 1% and had contracted 0.2mm from the first stage, -- receiving -- C and D -- formation -- it was extended 1.0mm from the front and having been extended 0.5mm was observed from the first stage.

[0024] When shifting to recrystallized structure partially from the above thing with heat in case the grid of the condition of a rolling organization is aging desiccation, it turns out that a grid carries out configuration change which is contracted in the height direction. Consequently, force which is strongly stuck to an active material and a grid works, and it is thought that a life improves by this. moreover, a plate -- formation -- although cubical expansion is caused behind, it is thought that the adhesion of a grid and an active material improves more conjointly with this.

[0025] In addition, the organization of the sheet in Cells A and B, i.e., a rolling organization, and the organization of the sheet in Cells C and D, i.e., the condition of being recrystallized structure partially, are shown in the mimetic diagram of drawing 3 . Moreover, although it doubles and the metal texture of the grid of each cell is shown in coincidence, it turns out that both are recrystallized structure partially.

(Experiment 2) this formation -- in order to investigate the effect by expansion of the active material at the time -- the formula of a paste -- changing -- formation -- the comparison by active material with which volume changes [ before and after ] differ was performed. The life test result of the cell E by which the life made the paste only from the lead powder which consists of usual plumbic acid ghost powder and metal lead powder on condition that the longest cell B, and the cell F which used the same paste on condition that Cell D sake [ comparison-] is shown in a table 2. E and F were short to the corresponding cells B and D, and the result of life test had the large fall of the life of E especially to B. although contraction of the plate of E and F was the same as B and D after aging desiccation when height change of a plate was measured -- formation -- next elongation -- formation -- it did not pass from a front to 0.5mm, i.e., about 0.5%. this -- formation -- when the cubical expansion of a next active material is 1% or more showed that it was more effective.

[0026]

[A table 2]

| 電池 N o | 極板の製造方法           | コーティング | 寿命回数    | 備考                    |
|--------|-------------------|--------|---------|-----------------------|
| E      | 圧延組織のまま<br>で格子に加工 | あり     | 4 0 0 0 | B, Dとペ<br>ーストが異<br>なる |
| F      | 再結晶組織後を<br>格子に加工  | あり     | 2 0 0 0 |                       |

[0027] In order to investigate in more detail, change of a life was investigated according to the presentation of a lead-calcium-tin system alloy. The result is shown in drawing 4 . The addition of tin and calcium shows that a life changes remarkably from this drawing. This is based on the corrosion resistance in each alloy presentation, and a mechanical strength. This drawing shows that 0.05 - 0.08% of range is suitable as a density range of calcium 0.5 to 2.0% as a density range of tin.

[0028] Moreover, by this invention, as stated above, in the state of the lead sheet, it was important in the rolling organization to have formed recrystallized structure in the state of a grid, but in order not to form recrystallized structure in the state of a lead sheet, it was confirmed in another experiment that it is also effective to perform strip processing at the temperature of 120 degrees C or less.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The mimetic diagram of the production process which rolls out a Pb-calcium-Sn alloy and produces a lead alloy sheet while coating the surface with a Pb-Sb-Sn alloy

[Drawing 2] The schematic diagram of the plate for lead accumulators obtained from said lead alloy sheet

[Drawing 3] The mimetic diagram showing the crystallized state of the lead alloy sheet used for each cell, and a grid bone

[Drawing 4] Property drawing showing the relation between calcium and Sn concentration, and the count of life test

[Description of Notations]

1 Slab Casting Machine

2 Slab made from Pb-calcium-Sn Alloy

3 Pb-Sb-Sn Alloy Foil

4 Rolling Mill

5 Lead Alloy Sheet

11 Plate

12 Expanded Metal Grating Bone

13 Pb-Sb-Sn Alloy Coating Layer

14 Pb-calcium-Sn Alloy Grid Bone

A Grid bone cross section

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[Translation done.]

\* NOTICES \*

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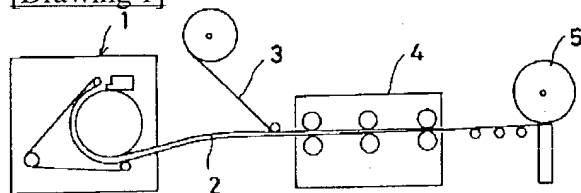
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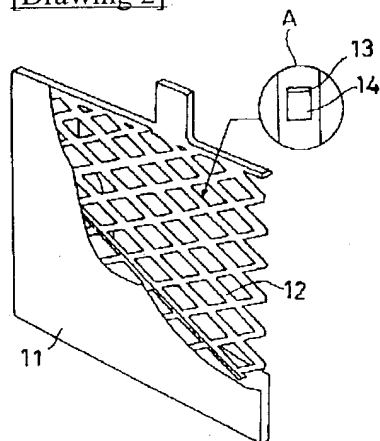
DRAWINGS

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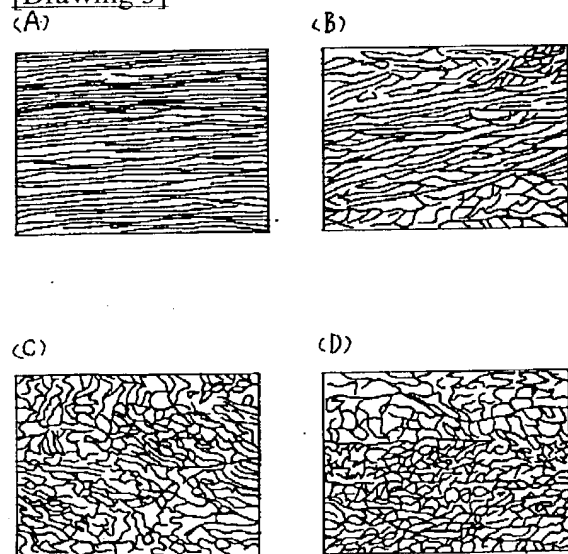
[Drawing 1]



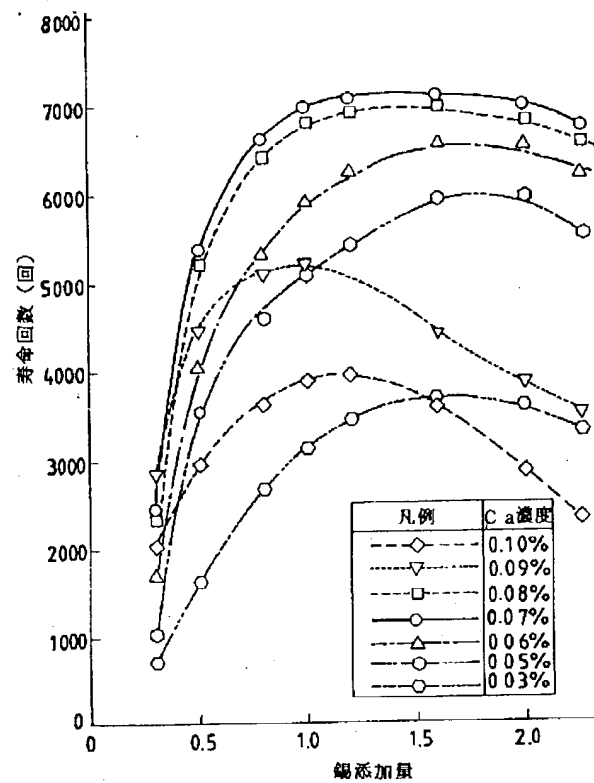
[Drawing 2]



[Drawing 3]



[Drawing 4]



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CORRECTION OR AMENDMENT

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[Official Gazette Type] Printing of amendment by the convention of 2 of Article 17 of patent law  
[Section partition] The 1st partition of the 7th section  
[Date of issue] December 24, Heisei 11 (1999)

[Publication No.] Publication number 6-267544  
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[Year copy format] Open patent official report 6-2676  
[Filing Number] Japanese Patent Application No. 5-51923  
[International Patent Classification (6th Edition)]

H01M 4/74  
4/14  
4/73

[FI]

H01M 4/74 B  
4/14 Q  
4/73 A

[Procedure revision]

[Filing Date] March 15, Heisei 11

[Procedure amendment 1]

[Document to be Amended] Specification

[Item(s) to be Amended] 0003

[Method of Amendment] Modification

[Proposed Amendment]

[0003] For the casting till then, and the method of carrying out expanded processing of the lead alloy sheet which rolled out such an alloy system in the cell used for a grid, and using as a grid object is large, and has spread.

[Procedure amendment 2]

[Document to be Amended] Specification

[Item(s) to be Amended] 0009

[Method of Amendment] Modification

[Proposed Amendment]

[0009]

[Means for Solving the Problem] A plate for lead accumulators of this invention cold-rolls slab of a lead-calcium-tin system alloy at temperature of 120 degrees C or less so that it may attain said purpose. Consider as a lead alloy sheet which has a precise rolling organization in the interior of an alloy, and before recrystallization, machine expanded processing etc. and this is made into a grid object. After being filled up with a paste used as an active material, some or all of the crystalline structure inside a grid alloy is made into recrystallized structure, and a lead accumulator of this invention uses said plate for lead accumulators as an anode plate.



[Procedure amendment 3]

[Document to be Amended] Specification

[Item(s) to be Amended] 0013

[Method of Amendment] Modification

[Proposed Amendment]

[0013] Moreover, as for said plate for lead accumulators, using as an anode plate is desirable. Moreover, a life can be raised more by giving a lead-antimony-tin system alloy to a part of surface of said lead alloy sheet, or surface.

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[Translation done.]